

(12) **UK Patent Application** (19) **GB** (11) **2 206 890** (13) **A**  
(43) Application published 18 Jan 1989

(21) Application No 8815708

(22) Date of filing 1 Jul 1988

(30) Priority data  
(31) 69350 (32) 2 Jul 1987 (33) US

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(51) INT CL<sup>4</sup>  
**B65D 65/38 // C08J 5/18**

(52) Domestic classification (Edition J):  
**C3V EF**  
**B8C W14**  
**C3W 207 208 209 217 219**  
**U1S 1425 1574 1814 2087.3043 3045 B8C C3V**

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**EP A 0244982** **EP A 0228818** **EP A 0168928**  
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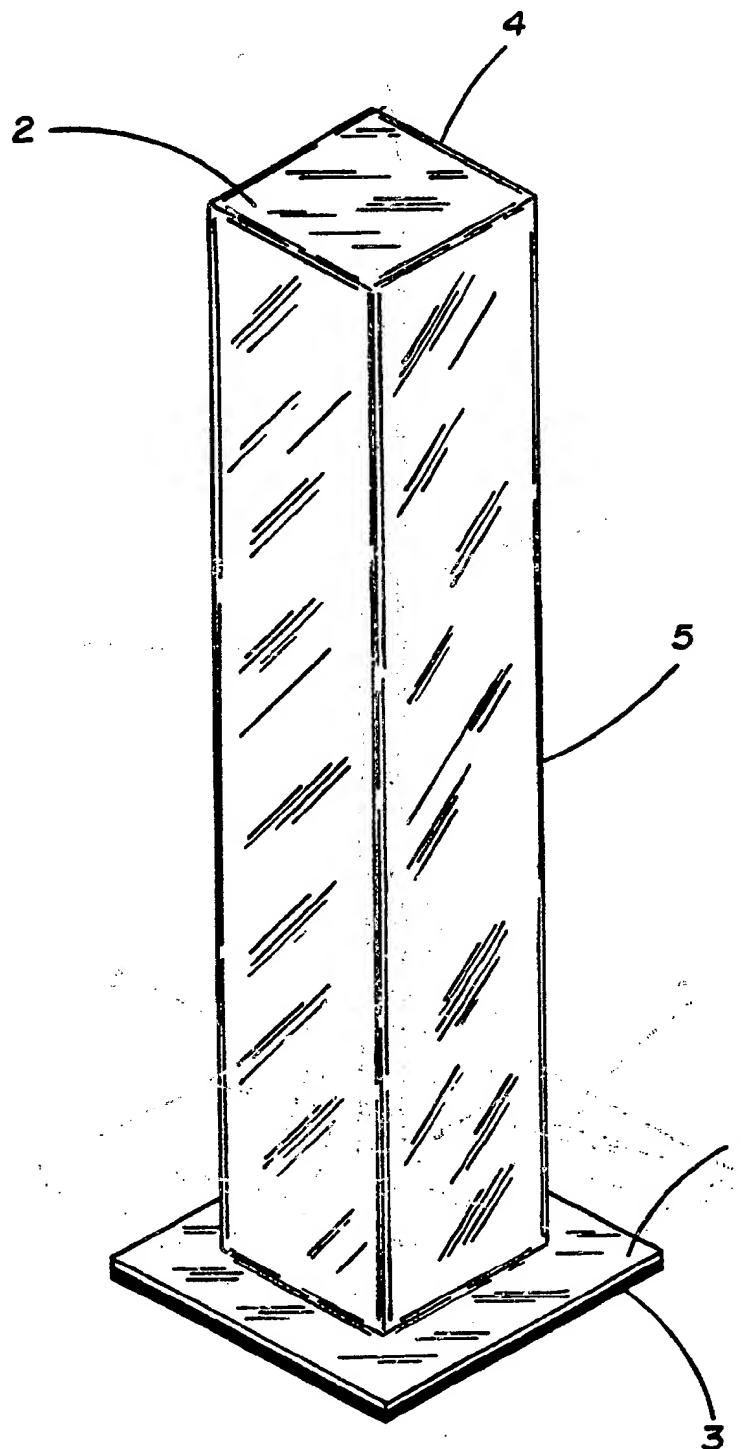
(58) Field of search  
**C3V**  
**B8K**  
**C3M**

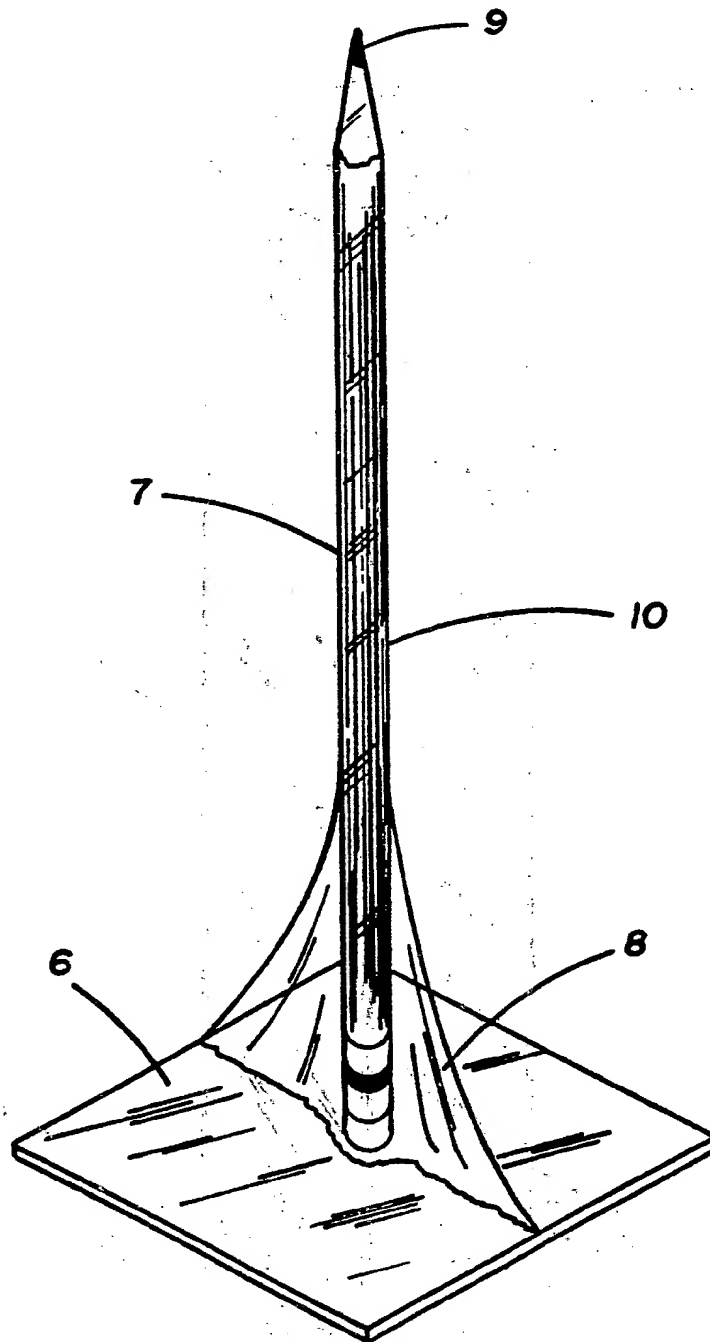
(54) **Skin package film**

(57) A skin packaging film, particularly suitable for skin packaging high profile and/or heavy articles, linear ethylene/alpha-olefin co-polymer. In one embodiment, the film is antistatic and may be employed for skin packaging of electro-static sensitive items such as circuit boards.

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FIG. 1

FIG. 2

- 1 -

## SKIN PACKAGE FILM

The present invention relates to a specific film as a skin package film for high-profile and/or heavy articles, both food and non-food items. More particularly the film comprises linear ethylene/alpha-olefin copolymer.

- 5 In a preferred embodiment, the film is antistatic or static dissipative, and may be employed for skin packaging electrostatic sensitive devices, such as circuit boards.

## BACKGROUND OF THE INVENTION

- Skin packaging is essentially a vacuum forming process. In a  
10 typical process, a sheet of thermoplastic film is placed in a frame, and below the frame is a vacuum plate upon which a piece of support pervious to gases such as a backing board is placed. The product to be skin packaged is positioned on top of the backing board and heat is applied to the thermo-  
15 sufficiently soft, the frame is lowered and the plastic sheet drapes itself over the product. As this happens, a partial vacuum is created through the vacuum plate and the air underneath the plastic film is withdrawn through the backing board. The air pressure differential between the top and the  
20 the product. The support is adapted to bond to the plastic sheet. Typically, the film may be thermally bonded to the support, or the film may be coated with a glue or the backing board may be so coated. Where the two contact each other, a strong bond is formed resulting in a package in which the product is tightly held to the support for safe shipping and for sub-  
25 sequent rack display in retail stores.

Vacuum skin packaging differs from the above described skin packaging process in that both the thermoplastic film and the support are impervious to gases and the resulting package can be evacuated and hermetically sealed, if desired. The same end result is sought, i.e. the product is to be tightly held by the film to the backing board. The vacuum skin packaging process generally employs a vacuum chamber with an open top. The product on an impervious backing board is placed on a platform within the vacuum chamber. The top of the chamber is then covered by a sheet of film which is clamped tightly against the chamber to form a vacuum type closure. The chamber is evacuated while the film is heated to forming and softening temperatures. The platform can then be raised to drive the product into the softened film and air pressure can be used above the film to force it tightly around the product.

The conventional method employs a backing board which is porous or which is perforated to make it pervious to gases so that the vacuum may be drawn directly through the backing board.

The term "vacuum" as used herein means a differential fluid pressure where the fluid can be either a gas or a liquid. The term "skin packaging" as used herein is intended to refer to vacuum packaging processes as described above, regardless of whether the support is pervious or impervious. Typically the support is made of a cardboard coated with adhesive polymer so that the film sheet will adhere as the sheet is heated and draped over the article being skin packaged and a differential pressure is applied.

Various patents describe skin packaging machinery and methods. Representative patents are French Pat. No. 1,258,357 (Bresson) (March 6, 1961), French Pat. No. 1,286,018 (Laroche Freres, Ltd.) (January 22, 1962), Australian Pat. No. 245,774 (Colbro Proprietary Ltd., and Cole and Son Proprietary Ltd.) (July 16, 1963), U.S. Pat. No. 3,491,504 (Young et al) (January 27, 1970), U.S. Pat. 3,545,163 (Mahaffy et al) (December 8, 1970), U.S. Pat. No. 3,694,991 (Perdue et al) (October 3, 1972), and U.S. Pat. No. 4,537,011 (Bortolani et al) (August 27, 1985). The disclosures of these patents are hereby incorporated by reference. However, it is noted that the film of the invention may be employed with various other types of skin

packaging machinery, such as the VS-44 marketed by the Cryovac Division of W. R. Grace or the PORT-A-VAC marketed by AmPak. The film of the invention is not intended to be limited to skin packaging employing only the machinery mentioned herein.

5 Skin packaging techniques are often disadvantageous in that an excess portion of film is undesirably wrinkled on evacuation and the packaged material or article becomes irregular in shape, thus producing a poor external appearance. In addition, the wrapping film is apt to be broken in the portions folded and wrinkled. It has been ascertained in  
10 actual practice that as the film thins in the course of the vacuum skin packaging process, conventional films, due to poor tensile strength and poor elongation, tend to be broken when subjected to high stretch or draw ratios at particular projections or recesses randomly arranged on the material being packaged. The breaking can occur during the packaging or  
15 afterwards during handling of the packaged product. Methods and films are thus unfavorable from a practical point of view. There is accordingly a strong demand for improvement in the packaging films and methods.

Conventional low density polyethylene (LDPE) is typically used for skin packaging, and attempts to provide specific improved skin packaging  
20 films have been made in the past. For instance, disclosed in U.S. Pat. No. 4,275,544 (Hisazumi et al assignors to Kureha) (June 30, 1981) is an improved method of vacuum packaging by using a specific laminated film as a package film, the laminated film being composed of a plastically deformable layer of a synthetic resin having a yield stress more than  $50 \text{ kg/cm}^2$  at a  
25 temperature of  $23^\circ\text{C}$ . and an elongation of less than 30% at elastic limit at a shaping temperature of  $50^\circ$  to  $180^\circ\text{C}$ . and an elastic layer of a synthetic resin having an elongation of more than 40% at elastic limit at the shaping temperature. Also, disclosed in U.S. Pat. 4,375,851 (Paulos assignor to Bemis) (March 8, 1983) is a skin packaging material composed of a film of  
30 thermoplastic material having a reinforcement consisting of strands (in the form of netting, or all extending in one direction parallel to one another) adapted on exposure for an appropriate time interval to a source of heat to have both the film and strands heat up to a forming temperature for being

skin packaged around an article on a substrate, with the strands less extensible than the film on equal heating of the film and strands, and the skin packaging of articles utilizing said material in such manner that the strands flare out from the article at the base of the article to provide a broader base of support for the article and to prevent undue thinning of the film. Also, it is known from U.S. Pat. 4,590,741 (Long et al assignors to General Dynamics) (May 27, 1986) to skin package electrostatically sensitive items with a 3-layer film including first and second outer layers of heat-sealable, electrically semi-conductive polyethylene each having a surface resistivity exceeding  $1 \times 10^{16}$  ohms per square, and a middle layer of heat-sealable polyethylene sandwiched between and bonded to said first and second outer layers and impregnated with a sloughable, electrically-conductive material providing said middle layer with a volume resistivity no more than  $1 \times 10^3$  ohms per centimeter, wherein said electrically-conductive material is prevented from sloughing to contaminate said item by said first or said second semiconductive polyethylene layer.

Accordingly, an object of this invention is to provide a suitable film for skin packaging of products, which film exhibits high tensile strength and elongation properties even at high stretch or draw ratios, whereby it is sufficiently deformable so that it can conform to the shape of the high-profile and/or heavy product being packaged by deformation without breaking. In other words, the film possesses an excellent deep draw feature affording a high draw ratio. It is another object of this invention to provide a skin packaging film for packing high profile and/or heavy products which film has antistatic characteristics. Thus, it is an aspect of the film that the film serves well as a material for packaging articles which typically have sharp projections such as bone-in meat, electronic components, and the like. The films in accordance with the present invention also typically have excellent see-through properties which is advantageous for reading code numbers preprinted on a product wrapped with the film. The films often exhibit very good adhesion to the support, particularly thermal bonding when the support is surlyn-coated cardboard.

# SUMMARY OF THE INVENTION

Therefore, the present invention provides a skin packaging film comprising linear ethylene/alpha-olefin copolymer.

5 The present invention also provides a skin package comprising a support of a material adapted for bonding to one face thereof of a polymeric film, an article on said face of the support, and a polymeric film comprising linear ethylene/alpha-olefin copolymer.

10 The present invention also provides a skin packaging process comprising: a) placing an article to be packaged on a support; b) positioning a film of linear ethylene/alpha-olefin copolymer above said article and support; c) heating the film; d) evacuating gases from the space between said film and said support; and e) sealing said film against said support.

15 The present invention also provides a skin packaging film comprising linear ethylene/alpha-olefin copolymer, said film being suitable for skin packaging high profile or heavy articles.

20 The present invention also provides a skin package comprising a support of a material adapted for bonding to one face thereof of a polymeric film, an article on said face of the support and a polymeric film comprising linear ethylene/alpha-olefin copolymer, said film being sufficiently deformable whereby high profile or heavy articles can be skin packaged with the film.

25 The present invention also provides a skin packaging process for packaging an electro-statically sensitive item comprising: a) placing the item to be packaged on a support; b) positioning a film above said item; c) heating the film d) drawing a vacuum between said film and said support; and e) drawing the film over and around the item forming a heat seal with the support; f) wherein said film comprises an antistatic linear ethylene/alpha-olefin copolymer film.



The present invention also provides an antistatic skin packaging film comprising antistatic linear ethylene/alpha-olefin copolymer.

It is a feature of the film of the invention that it has a high draw ratio of about 20:1 or higher and thus can be employed to skin package  
5 high profile objects.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic representation of a skin packaged, high profile object of rectangular cross-section in the direction horizontal to the support.

10 FIG. 2 is a schematic representation of a skin packaged, high profile sharpened pencil.

#### DETAILED DESCRIPTION OF THE INVENTION

The film of the present invention exhibits excellent draw ratios and stretch whereby it is sufficiently deformable so that it can be employed to skin package high profile and/or heavy objects. By "heavy", it is  
15 intended to mean objects having a weight of about 10 pounds (about 22 kg) or more, more preferably about 15 pounds (about 33 kg) or more, more preferably about 20 pounds (44 kg) or more. By "high profile", it is intended to mean objects having a vertical dimension:minimum horizontal dimension ratio of  
20 about 20:1 or more, for instance, an essentially cylindrical object having a height of about 20 inches (50.8 cm) in the direction substantially vertical (i.e. substantially perpendicular) to the support and a base diameter of about 1 inch (2.5 cm) in the direction substantially horizontal to the support. The film exhibits an excellent deepdraw, and will skin package  
25 objects with a draw ratio of the vertical dimension:minimum horizontal dimension of the object of about 20:1 or higher, more preferably above about 25:1, most preferably above about 30:1. In a preferred embodiment as

illustrated in Example I f) below, the deep draw ratio is about 64:1. Conventional LDPE works at 16:1 as can be seen in Table IIIB below, but splits at 26:1, as can be seen in Table IIIC below. Of course, the film of the invention can be employed, if desired, to skin package objects of lesser weight or shallow profile objects.

The film of the present invention comprises the polyethylene, linear ethylene/alpha-olefin copolymer. The linear ethylene/alpha-olefin copolymer may be blended with one or more suitable other polymers. Suitable other polymers are further described below. The term "linear low density polyethylene" (LLDPE) as used herein, for the linear ethylene/alpha-olefin employed in the present invention, refers to the newer copolymers of ethylene with one or more comonomers selected from C<sub>4</sub> to C<sub>10</sub> alpha olefins such as butene-1, pentene-1, 4-methyl-pentene-1, hexene-1, octene-1, etc. in which the molecules thereof comprise long chains with few side chains branches or cross-linked structures achieved by low pressure polymerization. The side branching which is present will be short as compared to non-linear polyethylenes. The molecular chains of a linear polymer may be intertwined, but the forces tending to hold the molecules together are physical rather than chemical and thus may be weakened by energy applied in the form of heat. Linear low density polyethylene has a density preferably in the range of from about 0.911 g/cc to about 0.928 g/cc for film making purposes. The melt flow index of linear low density polyethylene generally ranges from about 0.1 to about 10 grams per ten minutes and preferably between from about 0.5 to about 3.0 grams per ten minutes. Linear low density polyethylene resins of this type are commercially available and are manufactured in low pressure vapor phase and liquid phase processes using transition metal catalysts. Also, very low density linear low density polyethylenes (VLDPE) may be employed, and such typically have a density from about 0.910 g/cc to about 0.860 g/cc, or even lower.

Suitable other polymers which may be blended with the linear ethylene/alpha-olefin include, but are not limited to, polyethylenes other than linear ethylene/alpha olefins, ethylene vinyl acetates, and ethylene alkyl acrylates. Polyethylenes having densities ranging from about 0.900 g/cc to about 0.928 g/cc are called low density polyethylenes (LDPE) while those having densities from about 0.929 g/cc to about 0.940 g/cc are called

medium density polyethylenes (MDPE), and those having densities from about 0.941 g/cc to about 0.965 g/cc and over are called high density polyethylenes (HDPE). The older, classic low density types of polyethylenes are usually polymerized at high pressures and temperatures whereas the older, classic high density types are usually polymerized at relatively low temperatures and pressures. Ethylene vinyl acetate copolymers (EVA) are formed from ethylene and vinyl acetate monomers wherein the ethylene derived units in the copolymer are present in major amounts and the vinyl acetate derived units in the copolymer are present in minor amounts. For film forming purposes, it is desirable that the VA content of the EVA be from about 3% to about 25% as when an EVA has a higher VA content the EVA behaves more like a glue or adhesive. Ethylene alkyl acrylate copolymers (EAA) refers to copolymers formed from ethylene and alkyl acrylate wherein the ethylene derived units in the copolymer are present in major amounts and the alkyl acrylate derived units in the copolymer are present in minor amounts. Thus, the term "ethylene-methyl acrylate copolymer" (EMA) refers to a copolymer formed from ethylene and methylacrylate monomers. The term "ethylene-ethylacrylate copolymer (EAA) refers to a copolymer formed from ethylene and ethyl acrylate monomers. The term "ethylene-butyl acrylate copolymer" (EBA) refers to a copolymer formed from ethylene and butyl acrylate monomers. Many suitable EBA's are commercially available and these have a butyl acrylate content from about 3% to about 18% by weight.

Also suitable for blending are copolymers of an alpha-olefin of the formula  $RHC=CH_2$  wherein R is H or  $C_1$  to  $C_8$  alkyl and an alpha,beta-ethylenically unsaturated carboxylic acid, and the like. Preferably, in the  $RHC=CH_2$  copolymer of an olefin and a carboxylic acid, the olefin is ethylene and the carboxylic acid is acrylic acid or methacrylic acid. Materials, which are the copolymer of an alpha-olefin having the formula  $RHC=CH_2$  wherein R is H or  $C_1$  to  $C_8$  alkyl and an alpha,beta-ethylenically unsaturated carboxylic acid, representatively may be one of the Nucrel (TM) polymers supplied by du Pont or may be one of the Primacor (TM) polymers, supplied by Dow Chemical Company, Midland, Michigan. These are produced by the copolymerization of ethylene and a carboxylic acid comonomer therefor such as acrylic acid or methacrylic acid. Also, the copolymer of an alpha-olefin having the formula  $RHC=CH_2$  wherein R is H or  $C_1$  to  $C_8$  alkyl and an alpha,beta-ethylenically unsaturated carboxylic acid may be metal salt

neutralized such as with sodium, Na. Thus, the copolymer may be an ionomer. Representatively, such an ionomeric material is commercially available as Surlyn (TM) from the E. I. du Pont de Nemours Company of Wilmington, Delaware, and is described in detail in U. S. Patent 3,355,319 and U. S. Patent 3,845,163.

In the preferred embodiment, the film is antistatic or static dissipative, and may be employed for skin packaging of electrostatic sensitive items such as circuit boards. Nevertheless, this embodiment of the film is also suitable for skin packaging of other products that do not need antistatic protection, such as pork, red meat, cartons of cottage cheese, boxed toys wherein one side of the box is open for viewing the toy through the plastic film skin package, and the like.

In the antistatic embodiment, the polymer contains less than about 20 percent by weight, more preferably less than about 15 percent by weight, of one or more antistatic agents. The agent(s) will generally increase the conductivity of the polymer (polymers are typically excellent insulators) by an order of magnitude up to several orders of magnitude. There is no particular method required for incorporating an agent into the polymer, and any of the well-known solvent "wet" blending, melt blending, or dry blending methods may be employed.

This antistatic embodiment may be exhibited by the ability of the polymeric film containing the agent to promote static charge decay, i.e. to dissipate a static charge. The film of polymer containing the agent is able to dissipate 99% of an applied static charge of  $\pm 5000$  volts direct current in a short amount of time, i.e. less than 20, more preferably less than 5, most preferably less than 2 seconds (2000 milliseconds).

The Department of Defense (DOD) and the Electronics Industry Association (EIA) each have their own standards on surface resistivity of a material in ohms/square as follows:

SURFACE RESISTIVITY RANGES

	<u>Insulative</u>	<u>Antistatic</u>	<u>Static Dissipative</u>	<u>Conductive</u>
DOD	Greater Than $10^{14}$	$10^{14}$ to $10^9$	$10^9$ to $10^5$	Less Than $10^5$
5 EIA	Greater Than $10^{13}$	$10^{13}$ to $10^5$		Less Than $10^5$

As can be seen, there are two main differences. One is that EIA defines insulative as above about  $10^{13}$  ohms/square, whereas DOD defines insulative as above about  $10^{14}$  ohms/square. The other difference is that EIA has one range of about  $10^{13}$  to about  $10^5$  ohms/square as antistatic, which results in antistatic being synonymous with static dissipative. On the other hand, DOD divides this into two separate ranges of about  $10^{14}$  to about  $10^9$  ohms/square for antistatic and about  $10^9$  to about  $10^5$  ohms/square for static dissipative. Frequently the literature, especially older literature, equates antistatic with static dissipative in discussions about static electricity.

Thus, the term "antistatic" as used herein describes material having a surface resistivity in the range of about  $10^9$  to  $10^{14}$  ohms/square (Department of Defense standard) and/or a material which can dissipate 99% of an applied static charge of  $\pm 5000$  volts direct current in a short amount of time, preferably less than about 20 seconds, more preferably less than about 5 seconds, most preferably less than about 2 seconds (Federal Test Method Standard 101C, Method 4046.1, "Electrostatic Properties of Materials"), and/or a material having a surface resistivity in the range of about  $10^5$  to  $10^{13}$  ohms/square (an alternative standard of the Electronics Industry Association).

The antistatic agents useful in the preferred embodiment of the present invention may be selected from (a) one or more fatty acid esters of polyhydroxy alcohols, (b) one or more polyalkoxylated compounds (i.e. polyethers) such as polyethylene oxides, polypropylene oxides, polybutylene oxides, polytetramethylene oxides, the reaction products of polyalkoxylates with long chain acids, the reaction products of polyalkoxylates with long chain alcohols, the reaction products of polyalkoxylates with long chain acid esters of polyhydroxyl alcohols (for instance polyalkoxylate reaction

products of long chain acids, of fatty glycols, of fatty sorbitols, of fatty sorbitans, and of fatty alcohols), or a mixture thereof, or a mixture of (a) and (b). Suitable long chains in either (a) or (b) are desirably from about C<sub>8</sub> to about C<sub>20</sub> or higher. The polyether chains in the suitable poly-  
5 alkoxyated compounds are of the formula  $(-OC_xH_{2x}-)_n$  wherein x is from 2 to about 8, wherein the alkyl group is straight or branched, and wherein n is from 2 to about 1000. Each agent will work by itself in a polymeric composition, as such antistatic compositions exhibit excellent static decay times; however, the combination of agents (a) and (b) in a polymeric composition is more desirable as these antistatic compositions display even  
10 shorter static decay times. Desirable fatty acid ester substituted polyhydroxy alcohols include, but are not limited to, the polyhydroxy alcohols selected from the C<sub>2</sub> to C<sub>6</sub> alcohols, such as ethylene glycol, 1,3-propylene glycol, 1,2-propylene glycol, 1,2-butanediol, meso-2,3-butanediol,  
15 1,4-butanediol, pinacol, pentaerythritol, 1,2,3,4,5-pentanepentol, sorbitan, or sorbitol, which polyhydroxy alcohol has been substituted with one or more fatty acid ester groups. A very desirable fatty acid ester substituted polyhydroxy alcohol is glycerol monostearate (GMS). A desirable polyether is polyethylene oxide (PEO), such as that sold by Union Carbide  
20 under the trade name Polyox, or is polytetramethylene oxide, such as that sold by du Pont under the trade name Terathane. A very desirable polyalkoxylate of a fatty alcohol is a polyethoxylated cetyl alcohol (PECA), as represented by the formula  $C_{16}H_{33}-O(-C_2H_4-O-)_nH$  wherein n is from 2 to about 50. A very desirable antistatic film comprising linear ethylene/alpha-  
25 olefin copolymer contains GMS, PEO, and PECA.

Advantageously, the admixture of polymer and antistatic agent also includes a small amount of about 10% by weight or less, more desirably about 7% by weight or less of an antiblock, to help alleviate any tactile tackiness. A suitable antiblock is the siloid present in EPE 8160 supplied  
30 by Teknor Apex.

Manufacturing of films may be accomplished as follows. The film may be formed from non-orientable material or, if formed from an orientable (i.e. heat-shrinkable) material may be formed from a tube by using a "trapped bubble" technique commonly known as the "hot blown" technique. In  
35 forming a hot blown film, the tube is first stretched by a hot blown bubble

essentially immediately after extrusion while the tube is still at an elevated temperature above the orientation temperature range of the material. Thereafter, the film is cooled, by well-known methods. Those of skill in the art are well familiar with this process and the fact that the resulting film has substantially unoriented characteristics. Other methods for forming unoriented films are well known. Exemplary, are the planar methods of slot die extrusion or cast extrusion which, likewise, are well known to those in the art. If an oriented, i.e. heat-shrinkable, film is desired, the manufacture may be generally accomplished by extrusion (single layer films) or coextrusion (multi-layer films) of thermoplastic resinous materials which have been heated to or above their flow or melting point from an extrusion or coextrusion die in, for example, either tubular or planar (sheet) form, followed by a post extrusion cooling. The stretching for orientation may be conducted at some point during the cool down while the film is still hot and at a temperature within its orientation temperature range, followed by completing the cooling. Alternatively, after the post extrusion cooling, the relatively thick "tape" extrudate is then reheated to a temperature within its orientation temperature range and stretched, to orient or align the crystallites and/or molecules of the material and then cooled down. An "oriented" or "heat shrinkable" material is defined herein as a material which, when heated to an appropriate temperature above room temperature (for example 96°C), will have a free shrink of about 5% or greater in at least one linear direction.

Many other process variations for forming films are well known to those in the art. For example, conventional thermoforming or laminating techniques may be employed. For instance, multiple substrate layers may be first coextruded via a blown bubble tube with additional layers thereafter being extrusion coated or laminated thereon, or two multi-layer tubes may be coextruded with one of the tubes thereafter being extrusion coated or laminated onto the other.

As used herein the term "extrusion" or the term "extruding" is intended to include extrusion, coextrusion, extrusion coating, or combinations thereof, whether by tubular methods, planar methods, or combinations thereof.

If desired, the film of the invention may contain a barrier layer. The barrier layer may be composed of a layer comprising vinylidene chloride copolymer (saran), or composed of a layer comprising hydrolyzed ethylene-vinyl acetate copolymer (EVOH), preferably hydrolyzed to at least about 50%,  
5 most preferably to greater than about 99%, or composed of both a layer comprising vinylidene chloride copolymer and a layer comprising EVOH. When the barrier layer is composed of a layer comprising EVOH, the mole percent of vinyl acetate prior to hydrolysis should be at least about 29%, since for  
10 lesser amounts the effectiveness of the hydrolyzed copolymer as a barrier to fluids such as gas is substantially diminished. It is further preferred that the barrier copolymer have a melt flow being generally compatible with that of the other components of the multi-layer film, preferably in the range of about 3-10 (melt flow being determined generally in accordance with ASTM D1238). The gas of main concern is oxygen and transmission is  
15 considered to be sufficiently low, i.e. the barrier material is relatively gas impermeable, when the transmission rate for the barrier material is below  $70 \text{ cc/m}^2/\text{mil thickness}/24 \text{ hours/atms}$ , as measured according to the procedures of ASTM Method D-1434. EVOH can be advantageously utilized in the film of the invention since irradiative high energy electron treatment of  
20 the fully coextruded film does not degrade an EVOH barrier layer, as could be the case of a vinylidene chloride copolymer barrier layer, as is further discussed below. This gas "impermeability" of barrier polymers such as Saran or EVOH as described in this paragraph is intended only to be a reference to barrier polymers. It is not intended to be a reference to the  
25 gas "impervious" characteristic of one kind of support used in skin packaging as described above, although in some skin packaging applications it may be desirable to employ a barrier polymeric film as the support.

Irradiation is not necessary, as very suitable films exhibiting an excellent deep draw and a high draw ratio can be obtained without  
30 irradiation. Irradiative cross-linking, if desired, may be accomplished by the use of high energy electrons, ultra-violet rays, X-rays, gamma rays, beta particles, etc. Preferably, electrons are employed up to about 20 megarads (MR) dosage. The irradiation source can be any electron beam generator operating in a range of about 150 kilovolts to about 6 megavolts  
35 with a power output capable of supplying the desired dosage. The voltage can be adjusted to appropriate levels which may be for example 1,000,000 or



2,000,000 or 3,000,000 or 6,000,000 or higher or lower. Many other apparatus for irradiating films are known to those of skill in the art. The irradiation is usually carried out at a dosage between about 1 MR and about 20 MR, with a preferred dosage range of about 2 MR to about 12 MR. 5 Irradiation can be carried out conveniently at room temperature, although higher and lower temperatures, for example, 0°C to 60°C may be employed.

Furthermore, those of skill in the art generally recognize that irradiation with high energy electrons is generally harmful to saran barrier layer compositions, as irradiation may degrade and discolor saran, making it 10 turn brownish. Thus, if full coextrusion followed by high energy electron irradiation of the multi-layer structure is carried out on a film having a barrier layer containing a saran layer, the irradiation should be done at low levels with care. Alternatively, this situation may be avoided by using extrusion coating. Accordingly, by means of extrusion coating, one may 15 first extrude or coextrude a first layer or layers, subject that layer or layers to high energy electron irradiation and thereafter extrusion coat the saran barrier layer and, for that matter, simultaneously or sequentially extrusion coat other later layers (which may or may not have been irradiated) onto the outer surface of the extruded previously irradiated 20 tube. This sequence allows for the high energy electron irradiative treatment of the first and later layer or layers without subjecting the saran barrier layer to the harmful discoloration effects thereof.

Cross-linking of the polymers may also be accomplished chemically through utilization of chemical cross-linking agents, as is well known to 25 those of skill in the art. For instance, cross-linking agents, such as organic peroxides or dialdehydes, have been used to cross-link polyethylene polymers and copolymers. A general discussion of chemical cross-linking can be found at pages 331 to 414 of volume 4 of the Encyclopedia of Polymer Science and Technology, Plastics, Resins, Rubbers, Fibers published by John 30 Wiley & Sons, Inc. and copyrighted in 1966.

DETAILED DESCRIPTION OF THE DRAWINGS

Referring to FIG. 1, a schematic view of an object 5 is shown skin packaged to a support 3. The object is of rectangular cross-section in the direction horizontal to the support. The support 3 is perforated Surlyn-coated cardboard (not shown). The film 4 goes from the top 2 of the object 5, down to wherein portion 1 of the film covers the support 3.

Referring to FIG. 2, a schematic view of a pencil 10 having sharpened point 9 is shown skin packaged with film 7 to support 6 with the point 9 in the direction away from support 6 and the eraser end adjacent support 6. The support 6 is Surlyn coated cardboard (not shown). Also shown is some webbing 8 of film 7 about 2/3 of the way down from point 9.

EXAMPLES

The following Examples illustrate the preferred embodiments of the invention. It is not intended to limit the invention thereby.

15 All percentages indicated in the Examples are percentages by weight, except the amount of Polyox was so small that it is indicated in parts per million (ppm).

The following materials were employed in the Examples;

20 Trycol (TM) 5984 is a polyethoxylated cetyl alcohol (PECA) supplied by Emery Industries.

Food grade (GMS) glyceryl monostearate CPH-53-N was supplied by C. P. Hall.

Alathon F-3445 is an EVA having about 3.5% vinyl acetate. It was supplied by du Pont.

Dow XU 61512.08L is a VLDPE supplied by Dow. The comonomer is octene; the melt index is 0.80, and the density is 0.905.

5 Dowlex (TM) 2045.04 is a linear low density polyethylene supplied by Dow Chemical Company, Midland, Michigan. It has a density of  $0.920 \pm 0.002$ ; the comonomer is octene; and the melt index is 1.1. Hereinafter, this is referred to as LLDPE.04 for brevity.

10 Dowlex (TM) 2045.03 is a linear low density polyethylene supplied by Dow Chemical Company, Midland, Michigan. It has a density of 0.920; the comonomer is octene; and the melt index is 1.1. Hereinafter, this is referred to as LLDPE.03 for brevity.

Chemplex 3404 is a LDPE supplied by Chemplex Company, Rolling Meadows, Illinois.

15 EPE 8160 clear concentrate antiblock is a micron sized silica which is a blend by weight of 90% LDPE (Dow Resin 722) with 10% Syloid 378. The syloid is an infrared opaquefier supplied by Teknor Apex.

Polyox (TM) is a polyethylene oxide (PEO) sold by Union Carbide.

#### EXAMPLE I

20 Using the method of slot die extrusion with a Pacemaker 3.5 inch (8.9 cm) slot die extruder supplied by National Rubber Manufacturers, a 20 mil (0.51 mm) thick film was made having the following composition:

DR  
D'

TABLE I

<u>Ingredient (%)</u>		<u>PERCENTAGES</u>		
	LLDPE.04	98.5)		)
	PECA	1.0)	90%	)
5	GMS	0.5)		) 100%
	PEO	200 ppm)		)
	EPE 8160		10%	)

Next, using skin packing machines supplied by AmPak, the following items were skin packaged with the film using a Surllyn-coated perforated cardboard backing board as a support:

- a) wooden block of 2-7/8 inches X 5 inches X 9 inches with the 9 inch length vertical to the cardboard; draw ratio was about 3.1:1;
- b) lead brick of 2 inches X 4 inches X 8 inches with the 2 inch thickness vertical to the cardboard; draw ratio was about 0.5:1;
- 15 c) cylindrical soda can of 3-5/8 inches diameter X 4-3/4 inches height with the 4-3/4 inch height vertical to the cardboard; draw ratio was about 2.3:1;
- d) circuit board of 5 inches wide X < inch thick X 6 inches long with the < inch thickness vertical to the board; draw ratio was about 12:1;
- 20 e) capacitor of 2-< inches diameter X 4> inches height with the 4> inch height vertical to the cardboard and the capacitor had < inch tall multiple pointed pin connectors pointing in the vertical direction; draw ratio was about 1.7:1;
- 25 f) pointed wooden stick of 1/8 inch diameter X 8< inches height with the 8< inches height vertical to the cardboard; draw ratio was about 64:1;

- g) pocket knife of about 3/16 inch X 6-3/4 inches height with the 6-3/4 inches height vertical to the cardboard and the exposed blade pointed up; draw ratio was about 36:1;
- 5 h) inductor can of 2< inches X 2 inches X 2 inches with a 2 inch thickness vertical to the cardboard and the can had pins pointing up; draw ratio was about 1:1.

For all of these, the film was observed during skin packaging to draw well over sharp points and corners, exhibiting excellent deep draw strength and elongation. The film did not split during the skin packaging. This is particularly noted for the pointed wooden stick which exhibited an extremely high draw ratio of about 64:1. The packaged lead brick was turned over and held upside down several times. Although the brick weighed about 26 pounds 10 ounces (about 12.1 kg), the film immobilized the brick firmly, exhibited excellent strength in packaging a heavy object, and did not rip.

15

#### EXAMPLE II

The film of Example I above was tested for its antistatic property. The ability of each sample to dissipate a static charge was measured using the procedure described in Federal Test Method Standard 101C, Method 4046.1, "Electro-static Properties of Materials" (change notice dated October 8, 1982) on a static decay meter. Such meters are commercially available, such as the 406C static decay meter supplied by Electrotech Systems, Inc. Except where differences are indicated, samples were equilibrated at about room temperature at less than about 15% relative humidity for about 24 hours. After equilibration, each was placed in a static decay meter at 72°-73° F. (22-23° C) and charged to ±5000 VDC (volts direct current) at less than about 15% relative humidity. The time for 99% of the charge to dissipate was then measured.

TABLE II

<u>Sample</u>	<u>Decay Time (milliseconds)</u>
Film by itself	725
Film skin packaged around wooden block	1585*

5 \*Decay time was tested on the side of the package from the tail axis

EXAMPLE III

Several 4-mil thick monolayer films were extruded by the hot blown method as described above. These films were as follows:

TABLE IIIA

	<u>FILM</u>	<u>POLYMER</u>	<u>EPE 8160</u>	<u>IRRAD (MR)</u>
10	A1	VLDPE 90Z	10Z	None
	A2	VLDPE 90Z	10Z	6
	A3	VLDPE 100Z		None
	A4	VLDPE 100Z		6
15	B1	LLDPE.03 90Z	10Z	None
	B2	LLDPE.03 90Z	10Z	6
	B3	LLDPE.03 100Z		None
	B4	LLDPE.03 100Z		6
	C1	LDPE 90Z	10Z	None
20	C2	LDPE 90Z	10Z	6
	C3	LDPE 100Z		None
	C4	LDPE 100Z		6
	D1	EVA 90Z	10Z	None
	D2	EVA 90Z	10Z	6
25	D3	EVA 100Z		None
	D4	EVA 100Z		6

Next, using an AmPak skin-packaging machine, various items were skin packaged. For draw ratios up to and including 7:1, stacks of cubic blocks were used; for draw ratios of 10:1 and above, rigid plastic cylinders were used. Ordinary children's wooden cubic blocks of about 1 inch x 1 inch x 1 inch (about 2.5 cm x 2.5 cm x 2.5 cm) were skin packaged with the various films to Surlyn-coated cardboard. Blocks were chosen because vertical stacking readily correlated to approximate draw ratio, i.e. a stack of 5 blocks was about a 5:1 draw ratio. At a ratio of 10:1, however, the AmPak machine did not have enough head room to continue with the blocks, so the rigid plastic cylinders were used. Deep draw for the particular draw ratio was rated as poor (the film split), good (the film did not split but did not draw tightly to the base) or excellent (the film drew tightly to the base and did not split). Adhesion was judged by relative cardboard fiber binding involvement of the Surlyn coated cardboard to the film when the film was pulled off the Surlyn-coated cardboard. The results are summarized in Table IIIB below:

TABLE IIIB

20	<u>FILM</u>	<u>DEEP DRAW RATIO</u>	<u>DEEP DRAW PERFORMANCE</u>			<u>ADHESION TO SURLYN-COATED CARDBOARD PERFORMANCE</u>
			<u>POOR</u>	<u>GOOD</u>	<u>EXCELLENT</u>	
	A1	3:1			x	NT*
		4:1			x	NT
		5:1			x	Sealed with few fibers bound
25		7:1			x	NT
		10:1			x	Sealed with few fibers bound
		12:1			x	Sealed with few fibers bound
30		14:1			x	Sealed with few fibers bound
		16:1			x	Sealed with few fibers bound
35	A2	3:1			x	NT
		4:1			x	NT
		5:1			x	Poor Sealing

FILM	DEEP DRAW RATIO	DEEP DRAW PERFORMANCE			ADHESION TO SURLYN-COATED CARDBOARD PERFORMANCE
		POOR	GOOD	EXCELLENT	
5	A3	3:1		x	NT*
		4:1		x	NT
		5:1		x	Sealed with few fibers bound
		7:1		x	NT
		10:1		x	Sealed with few fibers bound
10		12:1		x	Sealed with few fibers bound
		14:1		x	Sealed with few fibers bound
		16:1		x	Sealed with few fibers bound
	A4	3:1		x	NT
		4:1		x	NT
		5:1		x	Poor Sealing
20	B1	3:1		x	NT
		4:1		x	NT
		5:1		x	Poor with few fibers bound
25		7:1		x	NT
		10:1		x	Excellent with fibers bound
		12:1		x	Excellent with fibers bound
		14:1		x	Excellent with fibers bound
30		16:1		x	Excellent with fibers bound
35	B2	3:1		x	NT
		4:1		x	NT
		5:1		x	Very good with fibers bound
40	B3	3:1		x	NT
		4:1		x	NT
		5:1		x	Sealed with some fibers bound
		7:1		x	NT
		10:1		x	Excellent with fibers bound
45		12:1		x	Excellent with fibers bound
		14:1		x	Excellent with fibers bound
		16:1		x	Excellent with fibers bound



FILM	DEEP DRAW RATIO	DEEP DRAW PERFORMANCE			ADHESION TO SURLYN-COATED CARDBOARD PERFORMANCE
		POOR	GOOD	EXCELLENT	
5	B4			x	NT
				x	NT
				x	Sealed with some fibers bound
10	Comparison C1			x	NT
				x	NT
				x	Sealed with some fibers bound
15				x	NT
				x	Poor sealing
				x	Poor sealing
				x	Poor sealing
				x	Poor sealing
				x	Poor sealing
20	Comparison C2			x	NT
				x	NT
				x	Very good with fibers bound
				x	NT
				x	NT
25	Comparison C3			x	NT
				x	NT
				x	Poor with few fibers bound
				x	NT
				x	Poor sealing
30				x	Poor sealing
				x	Poor sealing
				x	Poor sealing
				x	Poor sealing
				x	Poor sealing
35	Comparison C4			x	NT
				x	NT
				x	Sealed with some fibers bound
40				x	NT
				x	NT
45	Comparison D1			x	NT
				x	NT
				x	Poor with few fibers bound

FILM	DEEP DRAW RATIO	DEEP DRAW PERFORMANCE			ADHESION TO SURLYN-COATED CARDBOARD PERFORMANCE
		POOR	GOOD	EXCELLENT	
5	Comparison D2				
	3:1		x		NT
	4:1		x		NT
	5:1		x		Poor with few fibers bound
	7:1		x		NT
10	Comparison D3				
	3:1		x		NT
	4:1	x			NT
	5:1	x			Poor with few fibers bound
15	Comparison D4				
	3:1		x		NT
	4:1		x		NT
	5:1		x		Poor with few fibers bound
20	7:1		x		NT

\*NT = Not Tested

As can be seen from Table IIIB, the deep draw ratio was excellent for VLDPE, LLDPE and LDPE (film samples A1 through C4), but only good or poor for EVA (film samples D1 through D4). Thus, the deep draw of the linear ethylene/alpha-olefin films of the invention was superior to that of EVA. Also, irradiation improved the adhesion to the Surllyn-coated cardboard for LLDPE, LDPE, and EVA.

Next, it was illustrated that the linear ethylene/alpha-olephin films of invention were superior to conventional LDPE films. With the VLDPE, LLDPE and LDPE (but not EVA) films, pencils (like that illustrated in FIG. 2 but not sharpened) were skin packaged in the vertical direction. The pencils had a diameter of about 0.29 inch (about 0.74 cm) and a height of about 7.5 inches (19.1 cm). The blunt, unsharpened end of the pencils was away from the cardboard and the eraser end was adjacent the cardboard. Webbing occurred about half way down the pencils. The results are summarized in Table IIIC below:

TABLE IIIC

<u>FILM</u>	<u>DEEP DRAW RATIO</u>	<u>DEEP DRAW PERFORMANCE</u>			<u>ADHESION TO SURLYN-COATED CARDBOARD PERFORMANCE</u>
		<u>POOR</u>	<u>GOOD</u>	<u>EXCELLENT</u>	
5 A1	26:1			x	Tacky but no fibers
A2*	26:1			x	Some fiber involvement
A3	26:1			x	Tacky but no fibers
A4*	26:1			x	Some fibers and card-board delamination
10 B1	26:1			x	Very modest fiber involvement
B2*	26:1			x	Some fiber involvement
B3	26:1			x	Very modest fiber involvement
15 B4*	26:1			x	Some fibers and card-board delamination
C1	attempted 26:1	x			Tacky but no fibers
C2*	attempted 26:1	x			Some fibers and card-board delamination
20 C3	attempted 26:1	x			Tacky but no fibers
C4*	attempted 26:1	x			Some fibers and card-board delamination

\*Irradiated at 6 MR.

25 All irradiated skin packaged pencils listed to an angle of about 20° to 30° from the cardboard base support. While it is not intended to be bound to any theory, it is believed this was due to the irradiation making the film so tough that it pulled the pencil instead of allowing it to remain substantially vertical.

30 All the LDPE film samples (C1 to C4) exhibited poor deep draw and ripped open at an attempted draw ratio of 26:1, whereas the VLDPE film samples (A1 to A4) and LLDPE film samples (B1 to B4) exhibited excellent deep draw at a draw ratio of 26:1. Thus the deep draw of the linear ethylene/alpha-olefin films of the invention is superior to that of conventional LDPE.

35 While certain representative embodiments and details have been shown for the purpose of illustration, numerous modifications to the formulations described above can be made without departing from the invention disclosed.

CLAIMS

1. A skin packaging film comprising linear ethylene/alpha-olefin copolymer.
2. The film of claim 1 having a draw ratio of about 20:1 or higher.
- 5 3. The film of claim 1, wherein said linear ethylene/alpha-olefin copolymer is in blend with a polymer which is compatible with said ethylene/alpha-olefin polymer and is selected from ethylene/alkyl-acrylate copolymer, high density polyethylene (HDPE), low density polyethylene (LDPE), ethylene/vinyl acetate (EVA), ethylene/propylene copolymers, and  
10 copolymers of an alpha-olefin having the formula  $RHC=CH_2$  where R is H or  $C_1$  to  $C_8$  alkyl and an alpha,beta-ethylenically unsaturated carboxylic acid, and mixtures thereof.
4. The film of claim 1, further including a barrier layer.
5. The film of claim 1, wherein said film has been irradiated at a  
15 dosage up to about 20 MR.
6. A skin package comprising a support of a material adapted for bonding to one face thereof of a polymeric film, an article on said face of the support, and a polymeric film comprising linear ethylene/alpha-olefin copolymer.
- 20 7. A skin packaging process comprising:
  - a) placing an article to be packaged on a support;
  - b) positioning a film of linear ethylene/alpha-olefin copolymer above said article and support;
  - c) heating the film;
  - 25 d) evacuating gases from the space between said film and said support; and

e) sealing said film against said support.

8. A skin packaging film comprising linear ethylene/alpha-olefin copolymer, said film being suitable for skin packaging high profile or heavy articles.

5 9. A skin package comprising a support of a material adapted for bonding to one face thereof of a polymeric film, an high-profile or heavy article on said face of the support and a polymeric film comprising linear ethylene/alpha-olefin copolymer deformed around the article and bound to the support.

10 10. An antistatic skin packaging film comprising antistatic linear ethylene/alpha-olefin copolymer.

11. The antistatic film of claim 10, said film being sufficiently deformable whereby high profile or heavy articles can be skin packaged with the film.

15 12. The antistatic film of claim 10 wherein said linear ethylene/alpha-olefin copolymer is in blend with one or more antistatic agents chosen from (a) one or more fatty acid esters of polyhydroxy alcohols, (b) one or more polyalkoxylated compounds, or a mixture of (a) and (b).

20 13. The antistatic film of claim 10 wherein said linear ethylene/alpha-olefin copolymer is in blend with glycerol monstearate, polyethoxylated cetyl alcohol, and polyethylene oxide.

14. The antistatic film of claim 10, wherein said film is able to dissipate an applied charge of  $\pm 5000$  volts direct current in about 2000 milliseconds or less.

25 15. A skin packaging process for packaging an electro-statically sensitive item comprising:

a) placing the item to be packaged on a support;

- b) positioning a film above said item;
- c) heating the film
- d) drawing a vacuum between said film and said support; and
- e) drawing the film over and around the item forming a heat seal with the support;
- f) wherein said film comprises an antistatic linear ethylene/alpha-olefin copolymer film.

16. The process of claim 15, said film being sufficiently deformable whereby high profile or heavy articles can be skin packaged with the film.

10 17. The process of claim 15 wherein said linear ethylene/alpha-olefin copolymer is in blend with one or more antistatic agents chosen from (a) one or more fatty acid esters of polyhydroxy alcohols, (b) one or more polyalkoxylated compounds, or a mixture of (a) and (b).

15 18. The process of claim 15 wherein said linear ethylene/alpha-olefin copolymer is in blend with glycerol monostearate, polyethoxylated cetyl alcohol, and polyethylene oxide.

19. The antistatic film of claim 15, wherein said film is able to dissipate an applied charge of  $\pm 5000$  volts direct current in about 2000 milliseconds or less.

20 20. A skin package comprising a support of a material adapted for thermal bonding to one face thereof of a polymeric film, an article on said face of the support, and a polymeric film wherein said film comprises antistatic linear ethylene/alpha-olefin copolymer.

## XP-002209446

AN - 1983-719427 [30]

A - [001] 013 028 034 036 04- 040 041 046 047 048 06- 066 067 075 09- 147  
15- 198 200 231 239 248 250 255 259 27& 289 303 311 318 325 336 339  
342 381 435 437 50& 512 514 516 523 532 536 54& 546 551 567 57& 573  
575 58& 580 59& 597 600 633 688 695 720 724

- [002] 013 028 034 036 04- 040 041 046 047 048 051 06- 066 067 075 09-  
147 15- 198 200 231 239 248 250 255 259 27& 289 303 311 318 325 336  
339 342 381 435 437 50& 512 514 516 523 532 536 54& 546 551 567 57&  
573 575 58& 580 59& 597 600 633 688 695 720 724

- [003] 013 028 034 036 04- 040 041 046 047 048 054 06- 066 067 075 09-  
147 15- 198 200 231 239 248 250 255 259 27& 289 303 311 318 325 336  
339 342 381 435 437 50& 512 514 516 523 532 536 54& 546 551 567 57&  
573 575 58& 580 59& 597 600 633 688 695 720 724 726

- [004] 013 028 034 036 04- 040 041 046 047 048 06- 066 067 075 09- 147  
15- 198 200 231 239 248 250 255 259 27& 289 303 311 318 325 336 339  
342 381 435 437 50& 512 514 516 523 532 536 54& 546 551 567 57& 573  
575 58& 580 59& 597 600 633 688 695 698 720 724

CPY - ELED

DC - A17 A94 Q34

FS - CPI;GMPI

IC - B65D65/02 ; C08L23/04

KS - 0002 0013 0037 0042 0206 0218 0222 0231 0234 0239 0241 0246 0257 0271  
0292 0789 1279 1590 1604 1985 1999 2011 2022 2271 2272 2277 2280 2281  
2307 2513 2562 2572 2595 2629 2635 2645 2780 3151 3155 3252 3257 3291  
3319 3320

MC - A04-G06A A08-M05 A08-S01 A12-S06

PA - (ELED) DENKI KAGAKU KOGYO KK

PN - JP58101133 A 19830616 DW198330 006pp

PR - JP19810198144-19811209

XA - C1983-070114

XIC - B65D-065/02 ; C08L-023/04

XP - N1983-129411

AB - J58101133 Stretch film comprises 100 wt.% low pressure (sic) and low density polyethylene having 0.905-0.940 g/cm<sup>3</sup> density and 1.2-3.5 g/10 mins. melt flow index, 2-40 wt.% adhesive tack agent, and 0.2-5 wt.% surfactant. The low pressure low density polyethylene is a copolymer of an ethylene (sic) and having less branch, and straight chain structure, and an alpha olefin such as 1-butene, 1-hexene, 1-octene, and methylpentene-1, etc., and the low pressure (sic) and low density polyethylene may be used with other low density polyethylene or ethylene-vinylacetate copolymer with wt. ratio 10-3/1-1. The adhesive tack agent is e.g., gum rosin, wood rosin, tall oil rosin, hydrogenated rosin, dimer rosin, and their glycerol ester, methylester, pentaerythritolester, and ethylene-glycol ester, EVA resin having 15-95 mole % vinylacetate, fatty acid 5C petroleum oil, aromatic 9C petroleum oil, or 5-9C copolymerisation petroleum oil. The surfactant is e.g., glycerine fatty acid ester, sorbitan fatty acid ester, sodium alkylsulphate, sodium alkyl-benzenesulphate, polyoxyethylene -polyoxypropylene block copolymer etc.

- The stretch film has excellent mechanical strength, elongation, resistance to frosting, transparency, and self-adhesiveness. No

migration of plasticiser to food stuff is observed with this film,  
therefore it is hygienic. Also there is no liberation of irritant  
odour when it is torn by melting or when it is burned.

IW - STRETCH FILM FOOD COMPRISE LOW DENSITY POLYETHYLENE CONTAIN TACK AGENT  
GUM ROSIN SURFACTANT SODIUM ALKYL SULPHATE  
IKW - STRETCH FILM FOOD COMPRISE LOW DENSITY POLYETHYLENE CONTAIN TACK AGENT  
GUM ROSIN SURFACTANT SODIUM ALKYL SULPHATE

NC - 001

OPD - 1981-12-09

ORD - 1983-06-16

PAW - (ELED ) DENKI KAGAKU KOGYO KK

TI - Stretch film for foodstuffs comprises low density polyethylene -  
contg. tack agent e.g. gum rosin and surfactant e.g.  
sodium-alkyl-sulphate